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Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Thiol-functionalized electrospun polyacrylonitrile nanofibrous membrane for highly efficient removal of mercury ions

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ARTICLE INFO

Article history:
Received 2 March 2016
Received in revised form 18 June 2016
Accepted 6 July 2016
Available online 15 July 2016

Keywords:
Electrospun
Thiol
Adsorption
Mercury

ABSTRACT

Mercury ions pollution has threatened people's health. Conventional nano-adsorbents suffer from the aggregation and later separation, novel adsorbent with high adsorption performance and easy recover properties is highly needed. In this study, thiol-functionalized electrospun polyacrylonitrile (PAN) nanofibrous membrane was obtained and used as easy recovery adsorbent for mercury ions. The morphologies and chemical composition were studied using SEM, TEM, ATR-FTIR, XRD and XPS. The results indicated that mercury adsorption performance was pH sensitive and the optimal pH range for mercury ions adsorption was about 5.5–6.0. The adsorption equilibrium reached within 25 min, and the adsorption process can be described using the pseudo-second-order model. Isotherm data fitted well to the Langmuir isotherm model. After adsorption of mercury ions, the thiol-functionalized nanofibrous membranes can be regenerated, and the adsorption efficiency maintained up to 90% after three times of usage.

1. Introduction

Mercury is considered as highly toxic and accumulative metal and it prone to cause serious damage to human. The toxicity of mercury strongly depends on its chemical form. Methylmercury is more toxic than other mercury species (such as inorganic mercury ions). However, the inorganic mercury ions are very easy to convert to methylmercury (Maramba et al., 2006). And most of mercury in wastewater exists in the form of mercury ions. Therefore, the removal of mercury ions is highly necessary.

Various methods have been used for the removal of mercury ions from aqueous solutions, including ion exchange (Oehmen et al., 2014), sulfurization (Fukuda et al., 2014), membrane separation (Tang et al., 2011; Zou et al., 2011) and adsorption (Hadi et al., 2015; Li et al., 2011b; Yonghui et al., 2015). Among these, adsorption is proved to be an efficient and cost-effective way. Many effective adsorbents have been developed for the adsorption removal of mercury ions. Active carbon (Li and Maroto-Valer, 2012; Li et al., 2012; Zhou et al., 2014), agriculture and industry waste (C. Namasivayam, 1997; Kadirvelu et al., 2004), natural rock (Ghassabzadeh et al., 2010), graphene (Li et al., 2013a), and hydrogels (Wang and Wang, 2010) have been used as adsorbents for the mercury ions from aqueous solutions. However, the recovery of these adsorbents after usage can be challenging and energy intensive since these adsorbents are micro or nano-scale particles. Therefore, developing adsorbents which can be separated from the solutions much easier are of highly importance.

Some researchers have referred that polymer membrane with great surface area and highly porous structure can be used as easily recover adsorbents (İpek et al., 2014; Saranya

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http://dx.doi.org/10.1016/j.cherd.2016.07.007

et al., 2015; Tang et al., 2011; Zou et al., 2011). Recently years, nanofibrous membranes whose surface area and porosity are much higher than the phase inversion prepared membranes have attracted more and more attentions due to its unique physic and chemical properties (Kumar et al., 2014). When used in adsorption process, nanofibrous membranes are much easier to be separated from the solutions which will make the adsorption process energy saving. Various functionalized nanofibrous membrane have been developed and used as adsorbents for heavy metal ions (Garifullin et al., 2013; Huang et al., 2014; Ma et al., 2013). Amino and carboxylic groups are widely used for the adsorption removal of Cu^{2+}, Pb^{2+}, and Ni^{2+} et al. (Deng et al., 2003; Wang et al., 2014a, 2015a, 2015b). Organic/inorganic hybrid nanofibrous membranes were also developed for treatment of heavy metal ions polluted waters with a slightly high selectivity toward to different metal ions (Luo et al., 2015). The selective adsorption of metal ions is mainly due to the difference of metal-ligand complex stability constant (Da'na and Sayari, 2012; Yasuhiro Shiraishi et al., 2002) As reported by the researchers (Bandaru et al., 2013; Javadian and Taghavi, 2014; Li et al., 2013b), thiol groups are highly effective for adsorption of mercury ions due to the high stability constant of thiol-mercury complex. However, thiol functionalized electrospun nanofibrous membrane for mercury ions adsorption was rarely reported in the literature (Wu et al., 2010). S. Wu and the coauthors used thiol-functionalized silica for the adsorption of copper ions. However, the adsorption capacity is limited by the amount of available thiol ligands.

In this study, thiol functionalized electrospun nanofibrous membrane was prepared aims to obtain a nanofibrous adsorbent with high adsorption performance for mercury ions and easy recover ability. Poly (glycidyl methacrylate) (PGMA) was firstly grafted on the surface of nanofibers because its large amount of epoxy groups in the side chain of PGMA. The epoxy groups were further transferred to thiol groups through episulfide treatment and ring opening reaction. Functionalization and adsorption processes were both studied in details.

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, M_w = 150,000), dimethylformamide (DMF), glycidyl methacrylate (GMA, 97%) were purchased from Sigma–Aldrich. GMA monomers were purified by passing through a column of neutral aluminum oxide to remove the inhibitors before use. Tris (hydroxymethyl) aminomethane (99+%) was purchased from ACROS Organics. Dopamine hydrochloride (99%), 2-bromoisobutyryl bromide (2-BIB, 97%) was purchased from Alfa Aesar. $Hg(NO_3)_2$, NaHS, tetrahydrofuran (THF), ammonia ($NH_3{\cdot}H_2O$) and triethylamine were commercially available from Sinopharm Chemical Reagent Co. Ltd. THF and triethylamine were distilled before use.

2.2. Thiol functionalization of PAN nanofibrous membrane

The PAN nanofibous membranes were prepared by electrospun method similar to our previous work (Wang et al., 2013b). The obtained PAN nanofibrous membranes were pre-coated by polydopamine (PDA), which can introduce hydroxyl groups (PAN@PDA) for further immobilization of 2-BIB (PAN@Br).

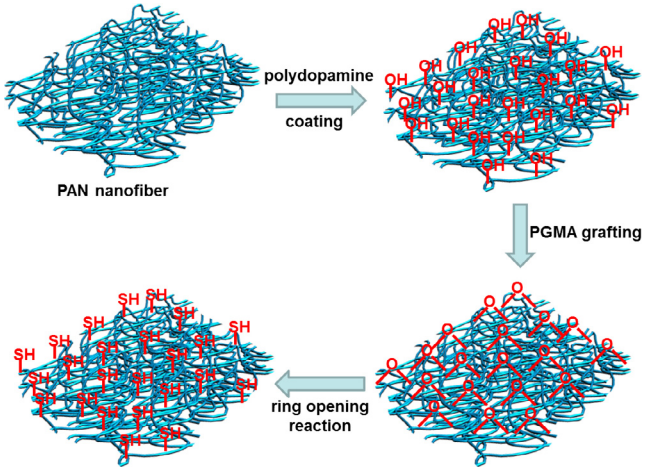

Fig. 1 – A preparation process for PAN@SH nanofibrous membrane.

The 2-BIB here worked as atom transfer radical polymerization initiator. After that, poly (glycidyl methacrylate) (PGMA) chains were grafted on the surface of PAN@Br nanofibers (PAN@PGMA). The surface modification process is reported in our previous work (Wang et al., 2014b).

Thiol functionalized PAN membranes were obtained by episulfide treatment and ring opening reaction. Typically, a piece of PAN@PGMA nanofibrous membrane was immersed into 20 mL ethanol, and then 5.0 g thiourea was added. The episulfide reaction was lasted for 6 h at 70 °C. The obtained PAN@S nanofibrous membranes were washed by deionized water until the solution became neutral. Finally, the PAN@S nanofibrous membranes were added into 100 mL deionized water, and then 2.0 g NaHS was added to start the ring opening reaction. The reaction was lasted for 12 h at 30 °C. The obtained PAN@SH nanofibrous membranes were washed by deionized water and dried. A preparation process for PAN@SH nanofibrous membrane was shown in Fig. 1.

2.3. Mercury ions adsorption and desorption experiments

$Hg(NO_3)_2$ was used as the source of mercury ions. 10 mg of dried PAN@SH nanofibrous membrane was added into 20.0 mL mercury ions solutions with different concentrations. The adsorption experiments were carried out in a thermostatic shaker bath for 12 h, operating at 25 °C and 100 rpm. The pH values of the solutions were adjusted by using 0.5 M HCl or NaOH solutions. The adsorption amount at time t (q_t) and equilibrium adsorption amount (q_e) were calculated from the following equations:

$$q_t = \frac{C_0 - C_t}{m} V \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

where C_0 is the initial concentration of mercury in solution (mg/L), C_e is the equilibrium concentration (mg/L), C_t is the concentration of mercury at time t (mg/L), q_e is the equilibrium adsorption capacity (mg/g), m is the mass of adsorbents (g), and V is the volume of solution (L), respectively.

Adsorption isotherm experiments were carried out at room temperature (25 °C) with the initial mercury ions concentrations ranging from 10 to 80 mg/L. The solution pH values were